EXAMINATION REPORT

Migration Study on Asphalt Modified with Rubber

Client: Degussa AG

Ordered on: June 20, 2005

Order number: 710-05

Test specimens: Prisms of dimension 40 x 40 x 160 mm

No. 25	Rubber-modified asphalt with Vestenamer (Splittmastix asphalt 0/8 S with GVmb 30/45)
No. 26	Rubber-modified asphalt (Splittmastix asphalt 0/8 S with GmB 30/45)
No. 27	Unmodified asphalt (Splittmastix asphalt 0/8 S with bitumen 30/45)

Contents

1. Objective

The use of additives in the production and processing of asphalt can result in additional groundwater pollution. The objective of the migration study is to determine the pollution of the groundwater caused by rubber-modified asphalt (Splittmastix asphalt 0/8 S with GVmB 30/45) when Vestenamer 8012 is used and to estimate the pollution based on an exposure scenario.

2. Summary

Migration studies were carried out in water to determine the potential pollution of groundwater when Vestenamer is used in rubber-modified asphalt. The migration test was conducted in conformity with DIN V 18035-7:2002-06. The asphalt test specimens (prisms dimensioned 40 x 40 x 160 mm) were subjected to a cold-water test at 23°C and a hot-water test at 60°. Three cycles with a stagnation time of 24 hours were conducted for each temperature. After each migration period, the test water was examined to determine the total migration of organic compounds (as measured by the TOC value, (total organic compounds)) and the specific migration of Vestenamer and its migratable components (oligomers). Furthermore, the parameters color, turbidity, tendency to foam formation and odor threshold (at 23°C) were measured in conjunction with the migration studies.

The studies that were carried out show that rubber-modified asphalt prisms containing Vestenamer (Specimen No. 25, GVmB) had a lower total migration of organic compounds (TOC values) in comparison with the rubber-modified asphalt prisms (Specimen No. 26, GmB) and the unmodified asphalt prisms (Specimen No. 27, mB). The migration from the asphalt prisms declines from cycle to cycle. The difference is particularly evident in the cold-water test (23°C, three cycles of 24 hours each): $TOC_{GVmB,25=(1x)}45/_{(2x)}34/_{(3x)}11$ mg/m^2 in comparison to $TOC_{GmB,26=(1x)}114/_{(2x)}68/_{(3x)}46$ mg/m^2 and $TOC_{mB,27=(1x)}89/_{(2x)}67/_{(3x)}34$ mg/m^2. The specific migration of Vestenamer and its oligomers out of the rubber-modified asphalt in water is below the analytic detection limit of 1 mg/m^2. Based on the experimental results, it must be concluded that the use of rubber in asphalt production tends to increase the total migration of organic compounds (TOC value). Addition of Vestenamer, however, results in distinctly lower total pollution of the groundwater from organic compounds migrating out of the asphalt, with and without rubber modification.

An estimate of the specific exposure of the groundwater by rainwater elution of the Vestenamer oligomers from the asphalt is possible only when the mass transfer taking place is combined with weather conditions. For the exposure estimate, the study resorted to a migration estimate based on a diffusion model in combination with meteorological data regarding precipitation frequency.

If we assume that pavement remains wet due to rain for a whole day at an average daily temperature of 20°C and that the rainwater is discharged continuously (worst case), then the contamination of the groundwater by the rainwater attributable to all Vestenamer

oligomers combined will equal 0.8 mg / m^2 of pavement per day. The estimated exposure is consistent with experimentally determined values.

If the rainwater stagnates on the pavement, the groundwater pollution will increasingly decline. Given the unrealistic assumption of complete stagnation over the entire day and an average precipitation of 10 mm per day, the groundwater pollution will turn out lower by 5 orders of magnitude and amount to 0.000013 mg / m^2 of pavement per day.

If we assume that a wet pavement heats up to approximately 60°C in one hour due to strong solar radiation, then, if there is a continuous discharge of rainwater from the pavement, the contamination of the groundwater from all Vestenamer oligomers combined will amount to 1.38 mg / m^2 of pavement per hour.

If we take into consideration the fact that no rain falls during 15 days in the month and assume that rain falls for approximately one hour during the 15 days per month that it does rain, then the average exposure of the groundwater due to all Vestenamer oligomers combined amounts to approximately 0.09 mg/m^2/day or 1.35 mg/m^2/month or 16.2 mg/m^2/year, respectively.

From the migration estimate, it is evident that the exposure of the groundwater from the elution of Vestenamer oligomers caused by rain is determined by the water solubility of the observed substances. Continuous discharge of the rainwater leads to higher elution rates, whereas stagnation phases result in lower elution rates. Moreover, the elution of Vestenamer oligomers caused by rain is approximately 4 times lower under winter conditions than under summertime meteorological conditions.

In regard to the total exposure of $TOC_{GmB,26=(1x)}$114 mg/m^2 of the groundwater through organic compounds from the rubber-modified asphalt, the use of Vestenamer in the manufacture of the asphalt leads to a reduction of about 60% in the total exposure of the groundwater from organic compounds, resulting in value of $TOC_{GVmB,25=(1x)}$ 45 mg/m^2. Under the most unfavorable conditions (continuous discharge of rainwater), the contribution of the Vestenamer itself is less than 2%. In the long term, the exposure of the groundwater from Vestenamer oligomers will continuously decline due to decreasing migration rates.

3.   Studies

3.1   Cold-water and hot-water test (total migration of organic compounds)

The migration test was carried out in conformity with DIN V 18035-7:2002-06. The asphalt prisms were subjected to a cold-water test at 23°C and a hot-water test at 60°C. Three cycles with a stagnation time of 24 hours were carried out for each temperature. After each migration period, the color, turbidity, and tendency to foam formation, odor threshold (at 23°C) and TOC value (total organic compounds) of the test water were examined. The surface to volume ratio amounted to 0.88 dm^{-1} for the migration test at 23°C and 1.44 dm^{-1} for the migration test at 60°C. The detection limit of the method was 0.1 mg/dm^2.

3.2   Specific migration of Vestenamer from the asphalt

One asphalt prism each of Specimens No. 25 and 26 was placed in a 500 ml graduated cylinder and covered with 300 ml of deionized water. The cylinder was sealed and kept at 20°C or 60°C, respectively. Three cycles with a stagnation time of 24 hours were carried out for each temperature. The water was shaken out three times with diethyl ether. The combined extracts were concentrated to a volume of 10 ml, provided with an internal standard (see 2.1) and analyzed by GC/MS. The surface to volume ratio amounted to 9.6 dm^{-1}. The detection limit was 10 $\mu g/dm^2$.

3.3   Determination of the low-molecular components of Vestenamer

To determine the low-molecular components, 0.25 g of Vestenamer was dissolved in 10 ml of hot toluene. The solution was kept in the refrigerator overnight and then membrane-filtered cold. The solution was diluted by a factor of 10 and analyzed on gas chromatographs with coupled mass spectrometers (GC/MS) and, after adding an internal standard (tridecane = C13), on gas chromatographs with flame ionization detectors (GC/FID).

3.4   Determination of the migration kinetics of Vestenamer out of the asphalt

One asphalt prism each of Specimens No. 25 and 26 was placed in a 500 ml graduated cylinder and covered with 300 ml of 95% ethanol. The cylinder was sealed and kept at 20°C or 60°C, respectively. Five milliliters were withdrawn after each of 3, 5, 10 and 21 days, provided with an internal standard (see 2.1) and analyzed by GC/MS. The surface to volume ratio was to 9.6 dm^{-1}.

4. Results

4.1 Cold-water and hot-water test (total migration of organic compounds)

4.1.1 Test condition 23°C

Test specimen	Asphalt	TOC Value		
	(#)	$[mg/dm^2]$		
	Cycle	1	2	3
25	GVmB	0.45	0.34	0.11
26	GmB	1.14	0.68	0.46
27	mB	0.89	0.67	0.34

(#) (G – rubber modified, V – Vestenamer, mB – bitumen)

4.1.2 Test condition 60°C

Test specimen	Asphalt	TOC Value		
	(#)	$[mg/dm^2]$		
	Cycle	1	2	3
25	GVmB	4.58	0.69	0.28
26	GmB	5.49	0.69	0.35
27	mB	4.10	0.80	0.63

(#) (G – rubber modified, V – Vestenamer, mB – bitumen)

4.2 Specific migration of Vestenamer from the asphalt

For both test temperatures, the migration of Vestenamer in water (test specimen 25) was below the detection limit of 10 µg / dm^2.

4.3 Determination of the low-molecular components of Vestenamer

4.3.1 Qualitative analysis

The qualitative analysis was performed on the GC/MS and the following chromatogram was obtained:

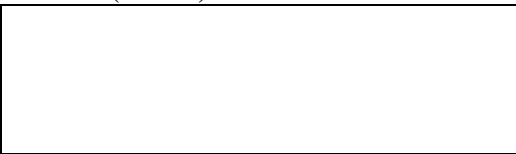The peaks labeled 1 to 5 have the follow mass spectra:

Peak 1 and 2 (dimer):

Molecular weight
M_W = 220 g/mol

Peak 3 (trimer):

Molecular weight
M_W = 330 g/mol

Peaks 5 and 6 (tetramer):

Molecular weight $M_W = 440$ g/mol

4.3.2 Quantitative analysis

The quantitative analysis was performed on the GC/FID and the following chromatogram was obtained:
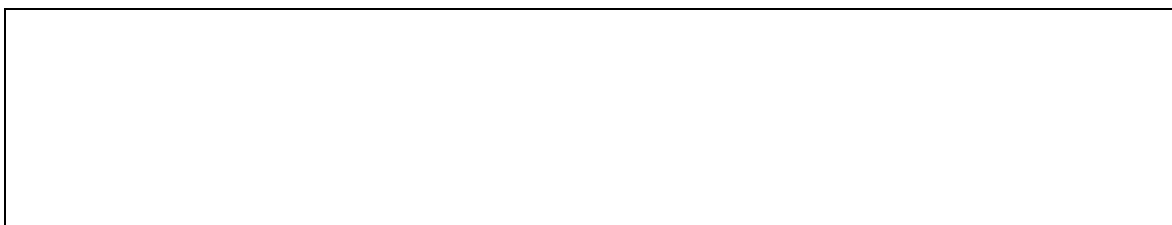
The low-molecular components (cyclooctene oligomers) were indirectly quantified using the added internal standard C13. The following results were determined:

	Vestenamer	
	[µg / ml]	[mg / g]
Dimers (peaks 1 + 2)	1.32	1.59
Trimer (peak 3)	8.48	3.40
Tetramers (peaks 4 + 5)	2.81	2.38

4.4 Determination of the migration kinetics

A quantification of the migration of Vestenamer oligomers was possible only at the contact conditions 60°C with 95% ethanol. To quantify peaks 1–3 (peaks 4 and 5 were below the detection limit), known quantities of Vestenamer solution from 2.1 were added to the blank sample of No. 26 and the concentrations in the corresponding migration solutions were determined on the bases of the regression lines obtained. Because of the very low transitions, analysis was performed on the specific m/z = 80.15.

The following table and chart summarize the results of the migration studies at 60°C:

60°C	3 days $[\mu g/dm^2]*$	5 days $[\mu g/dm^2]*$	10 days $[\mu g/dm^2]*$	21 days $[\mu g/dm^2]*$
Peak 1	7.6	12.6	14.1	24.1
Peak 2	16.6	20.8	24.3	42.8
Peak 3	46.4	61.6	73.2	112

*) The surface of one prism equals 2.88 /dm^2

5.   Analysis

The migration kinetics were based on a diffusion model. In other words, it was assumed that the release of the low-molecular Vestenamer oligomers from the rubber-modified asphalt obeys the Law of Diffusion. The change in the concentration over time is proportional to the change of the concentration over the path with the diffusion coefficient as proportionality constant (Fick's second law of diffusion, one-dimensional).

$$\frac{\partial c}{\partial t} = D \cdot \frac{\partial^2 c}{\partial x^2}$$

c – concentration
t – time
x – path
D – diffusion coefficient

The assumption is deemed as satisfied when the experimentally determined migration kinetics can be brought into agreement with the solution of the diffusion equation. The migration rate is determined by the diffusion coefficients of the low-molecular Vestenamer oligomers in the asphalt matrix and by their distribution (distribution coefficients) between asphalt and the contact medium, for example, rainwater or soil.

As can be seen in the following figure, the experimental points match the computed curves (solution of the diffusion equation) very well.

The diffusion coefficient is a macroscopic mass transfer variable with the mass unit cm^2/sec and generally can be expressed as follows:

$$D_P = D_0 \cdot e^{\frac{-E_A}{RT}}$$

The dependence of the diffusion coefficient on the temperature is of Arrhenius type. D_0 is a dimensionless proportionality constant, E_A the activation energy, R the universal gas constant R = 8.314 J/mol·K, and T is the temperature in kelvins.

The initial concentration of the Vestenamer oligomers in the asphalt was computed from the formulation of the asphalt mixture. It yielded 1.2 mg/kg for the dimers, 2.55 mg/kg for the trimers, and 1.8 mg/kg for the tetramers.

Accordingly, the diffusion coefficients of the Vestenamer oligomers at 60°C can be determined from the migration kinetics as follows: in the asphalt with dimer: $D_P = 8.1\ e^{-8}$ cm^2/sec, with the trimer: $D_P = 6.0\ e^{-8}\ cm^2$/sec.

The equation shown below postulates that the diffusion coefficient is correlated with the mobility of the matrix and the molecular weight of the migrant (as a substitute for the size of the molecule). This equation can be used to determine the matrix-specific constant (A_P value) from the experimentally determined diffusion coefficients.

$$D_P = D_0 \exp\left(A_P - 0.1351 \cdot M_r^{2/3} + 0.003 \cdot M_r - \frac{R \cdot 10454}{R \cdot T} \right)$$

D_P	-diffusion coefficient ($D_0 = 10^4\ cm^2$/sec)
$A_P = A_P' - \tau/T$	- *polymer*-specific constant
	(τ - material-specific temperature constant)
M_r	- relative molecular weight of the *migrant*
T	- *temperature* in K
$E_A = R \cdot 10454$	- reference activation energy
	$R \cdot 10454 = 86.9\ kJ$, R = 8,314 J/K·mol

For the rubber-modified asphalt, the equation yields a matrix-specific constant of $A_P = 10.2$ at a reference activation energy of 87 kJ/mol.

With the aid of the two variables, the diffusion coefficient of any Vestenamer oligomer in the asphalt matrix can be estimated at any desired temperature.

6. Exposure estimate
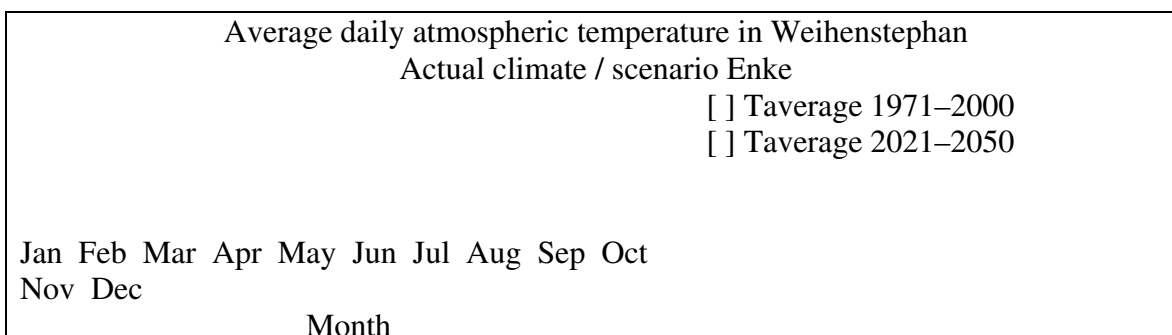
6.1 Meteorological conditions

The exposure estimate was calculated by using a migration estimate in combination with meteorological data regarding precipitation frequency. From the condensed report "Der Klimawandel in Bayern für den Zeitraum 2021–2050" [Climate change in Bavaria for the period 2021–2050] (knowledge level as of January 2005), it follows that approximately 15 dry days (precipitation less than 1 mm) and approximately 1 day with high precipitation (precipitation greater than 25 mm) are observed as the annual average. The average precipitation frequency for 1981 to 2000, expressed in days per month over an entire year, is compiled in the following figures, which were taken from the above condensed report.

Average number of days in the month with N < 1 mm
Meteorological Observatory Hohenpeissenberg (Enke)

[ ] days < 1 mm/day 1981–2000
[ ] days < 1 mm/d 2021–2050

Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec
                         Month

Average number of days in the month with N < 1 mm
Meteorological Observatory Hohenpeissenberg (Enke)

[ ] days >= 25 mm/year 1981–2000
[ ] days >= 25 mm/year 2021–2050

Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec
                         Month

Bayrisches Amt für Wasserwirtschaft (Bavarian Water Conservation Board)
"Der Klimawandel in Bayern für den Zeitraum 2021–2050"

The following figure, which was also taken from the above report, depicts the average daily atmospheric temperature over the course of a year.

<div style="border:1px solid black">

Average daily atmospheric temperature in Weihenstephan
Actual climate / scenario Enke

[ ] Taverage 1971–2000
[ ] Taverage 2021–2050

Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

Month

</div>

Bayrisches Amt für Wasserwirtschaft
"Der Klimawandel in Bayern für den Zeitraum 2021–2050"

6.2 Water solubility and distribution coefficient

For the substance-specific migration estimate based on a diffusion model, it is also necessary to know the distribution coefficient between asphalt and rainwater in addition to the diffusion coefficient. Since the kinetic migration studies from the asphalt were carried out in 95% ethanol, the asphalt/water distribution coefficient is not directly available as an experimental value. However, it is possible to estimate this coefficient using the octanol/water (K_{OW}) distribution coefficient and the water solubility of the observed substances.

The distribution coefficient of the Vestenamer oligomers between asphalt and rainwater was computed using the software "EPI Suite v3.12" of the US Environmental Protection Agency (EPA). The software may be downloaded from the following link: http://www.epa.gov/opptintr/exposure/docs/episuitedl.htm

For the exposure estimate, it is possible to use the octanol/water distribution coefficient as an approximation instead of the distribution coefficient between asphalt and rainwater. For a hydrocarbon with 16 carbon atoms (hexadecane and cyclohexadecene), we obtain the following octanol/water distribution coefficient and the water solubility at 25°C derived from it:

Water solubility Estimate from Log Kow (WSKOW v1.40)
     Water Solubility at 25 deg C (mg/L): 0.0009193
       log Kow used: 8.20 (estimated)
       no-melting pt equation used
     Water Sol (Exper. database match) = 0.0009 mg/L (25 deg C)
       Exper. Ref: SUTTON,C & CALDER,JA (1974)

6.3   Exposure estimate

The software MIGRATEST Lite was used for the migration estimate.

If we assume that the pavement is wet from rain through the entire day at an average daily temperature of 20°C with continuous discharge of rainwater (worst case), the total contamination of the groundwater by the rainwater attributable to all Vestenamer oligomers combined is equal to 800 µg / m^2 of pavement per day.

If the rainwater stagnates on the pavement, the groundwater pollution will be increasingly less. Given the unrealistic assumption of complete stagnation over the entire day and an average precipitation of 10 mm per day, the groundwater pollution will turn out lower by 5 orders of magnitude and amount to 0.013 µg / m^2 of pavement per day.

Given a wet pavement that sits for one hour at an average daily temperature of 20°C with continuous discharge of rainwater (worst case), then the contamination of the groundwater by the rainwater attributable to all Vestenamer oligomers combined will amount to 164 µg / m^2 of pavement per hour.

If the rainwater stagnates on the pavement, the groundwater pollution will increasingly decline. Given the unrealistic assumption of complete stagnation over the entire hour and an average precipitation of 10 mm per day, the groundwater pollution will turn out 10,000 times lower and amount to 0.013 µg / m^2 of pavement.

If we assume that a wet pavement heats up to approximately 60°C in one hour due to strong solar radiation, then, if there is a continuous discharge of rainwater from the pavement, the contamination of the groundwater from all Vestenamer oligomers combined will amount to 1,380 µg / m^2 of pavement per hour.

If we assume that a wet pavement heats up to approximately 60°C in one hour due to strong solar radiation, then, if the rainwater stagnates on the pavement, the contamination of the groundwater from all Vestenamer oligomers combined will amount to 0.013 µg / m^2 of pavement per hour.

If we observe the groundwater pollution during one hour of rain and continuous discharge of the rainwater (worst case) over the entire course of the year, then the affect of the average temperature during the given season can be clearly seen.

Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

Time [month]

If we take into consideration the fact that no rain falls during 15 days in the month and assume that rain falls for approximately one hour during the 15 days per month that it does rain, then the average exposure of the groundwater due to all Vestenamer oligomers combined amounts to approximately 90 µg/m^2/day or 1,350 µg/m^2/month or 16.2 mg/m^2/year, respectively.

7.   Conclusions

The studies that were conducted show that the rubber-modified asphalt prisms containing Vestenamer (Specimen No. 25) exhibit a lower total migration of organic compounds (TOC values) compared to the rubber-modified asphalt prisms (Specimen No. 26). The migration from the asphalt prisms declines from cycle to cycle. The difference is particularly evident in the cold-water test (23°C) over the three cycles (24 hours each): $TOC_{specimen25=(1x)}45/_{(2x)}34/_{(3x)}11$ mg/m^2 in comparison to $TOC_{specimen26=(1x)}114/_{(2x)}68/_{(3x)}46$ mg/m^2. The specific migration of Vestenamer and its low-molecular components out of the rubber-modified asphalt in water is below the analytic detection limit of 1 mg/m^2. Based on the experimental results, it must be concluded that the use of Vestenamer results in a lower total pollution of the groundwater from organic compounds migrating out of the asphalt.

A realistic migration of the Vestenamer and its low-molecular components in water can be obtained only by estimation. To make an exposure estimate for the migratable Vestenamer components, one must by all means determine the migration rate of the migratable Vestenamer components. The first experiments with water as test medium did not yield any measurable results and were traced back to the low water solubility of the low-molecular, migratable components of the Vestenamer. We therefore changed to a test medium (95% ethanol) with higher solubility for the migratable Vestenamer components. Of the five low-molecular components (oligomers) that could be detected in a toluene solution of Vestenamer, only the three components with the lowest molecular weight (peaks 1 to 3) exhibited a measurable migration in 95% ethanol.

The time-dependent migration studies made it possible, however, to verify the applicability of the laws relating to mass transfer and to determine molecule-specific variables, such as the diffusion coefficients of the Vestenamer oligomers, from the experimental results and, from those variables, to determine a matrix-specific constant (A$_P$ value), which is a measure for the internal mobility of the asphalt matrix. The temperature dependence of the mass transfer process can be taken into consideration using the reference activation energy (E$_A$). With the aid of the two variables, it is possible to estimate the diffusion coefficient of any Vestenamer oligomer in the asphalt matrix at any desired temperature.

For the substance-specific migration estimate based on a diffusion model, it is also necessary to know the distribution coefficient between asphalt and rainwater in addition to the diffusion coefficient. Since the kinetic migration studies from the asphalt were carried out in 95% ethanol, the asphalt/water distribution coefficient is not directly available as an experimental value. However, it is possible to estimate this coefficient using the octanol/water (K$_{OW}$) distribution coefficient and the water solubility of the observed substances.

An estimate of the exposure of the groundwater by rainwater elution of the Vestenamer oligomers from the asphalt is only possible when the mass transfer taking place is combined with weather conditions.

If we assume that pavement remains wet due to rain for a whole day at a temperature of 20°C and that the rainwater is discharged continuously (worst case), then the total contamination of the groundwater by the rainwater attributable to all Vestenamer oligomers combined will equal 800 µg / m^2 of pavement per day. The estimated exposure is consistent with experimentally determined values. The exposure of the groundwater from Vestenamer oligomers will continuously decline due to decreasing migration rates

If the rainwater stagnates on the pavement, the groundwater pollution will increasingly decline. Given the unrealistic assumption of complete stagnation over the entire day and an average precipitation of 10 mm per day, the groundwater pollution will turn out lower by five orders of magnitude and amount to 0.013 µg / m^2 of pavement per day.

Given a wet pavement that sits for one hour at an average daily temperature of 20°C with continuous discharge of rainwater (worst case), then the contamination of the groundwater by the rainwater attributable to all Vestenamer oligomers combined will amount to 164 µg / m^2 of pavement per hour.

If we assume that a wet pavement heats up to approximately 60°C in one hour due to strong solar radiation, then, if there is a continuous discharge of rainwater from the pavement, the contamination of the groundwater attributable to all Vestenamer oligomers combined will amount to 1,380 µg / m^2 of pavement per hour.

If we take into consideration the fact that no rain falls during 15 days in the month and assume that rain falls for approximately one hour during the 15 days per month that it does rain, then the average exposure of the groundwater due to all Vestenamer oligomers combined amounts to approximately 90 µg/m^2/day or 1,350 µg/m^2/month or 16.2 mg/m^2/year, respectively.

From the migration estimate, it is evident that the exposure of the groundwater from the elution of Vestenamer oligomers caused by rain is determined by the water solubility of the observed substances. Continuous discharge of the rainwater leads to higher elution rates, whereas stagnation phases result in lower elution rates. Moreover, the elution of Vestenamer oligomers caused by rain is approximately four times lower under winter conditions than under summertime meteorological conditions.

In regard to the total exposure of $TOC_{26=(1x)}$114 mg/m^2 of the groundwater through organic compounds from the rubber-modified asphalt, the use of Vestenamer in the manufacture of the asphalt leads to a reduction of about 60% in the total exposure of the groundwater from organic compounds, resulting in a value of $TOC_{V,25=(1x)}$ 45 mg/m^2. Under the most unfavorable conditions (continuous discharge of rainwater), the contribution of the Vestenamer itself is less than 2%. In the long term, the exposure of the groundwater from Vestenamer oligomers will continuously decline due to decreasing migration rates.

The results of the studies relate exclusively to the test specimens on which they are based.

Munich, December 23, 2005

FABES Forschungs-GmbH

Dr. Rainer Brandsch   Heike Benz

8.   Appendix 1

Report C-131535-05 of the Hygiene-Institut des Ruhrgebiets [Hygiene Institute of the Ruhr Region], dated September 7, 2005.

9.   Appendix 2

Report C-135028-05 of the Hygiene-Institut des Ruhrgebiets, dated December 22, 2005.